(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 870 819 A2

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
14.10.1998 Bulletin 1998/42

(51) Int Cl.[6]: **C10L 1/22**, C10L 1/14, C10L 10/00

(21) Application number: **98302812.7**

(22) Date of filing: **09.04.1998**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **10.04.1997 US 837246**

(71) Applicant: **ETHYL CORPORATION**
Richmond, Virginia 23219-4304 (US)

(72) Inventors:
- **Malfer, Dennis J.**
  Glen Allen, Virginia 23060 (US)
- **Franklin, Randall M.**
  Mechanicsville, Virginia 23116 (US)
- **Colucci, William L.**
  Glen Allen, Virginia 23060 (US)

(74) Representative: **Smaggasgale, Gillian Helen et al**
Mathys & Squire,
100 Gray's Inn Road
London WC1X 8AL (GB)

(54) Additives for minimizing intake valve deposits, and their use

(57) New, highly effective detergent/dispersants for use in spark ignition fuels are described. They are Mannich condensation products formed from (i) one mole part of at least one substituted hydroxyaromatic compound having on the ring both (a) an aliphatic hydrocarbyl substituent derived from a polyolefin having a number average molecular weight in the range of about 500 to about 3000, and (b) a C_{1-4} alkyl; (ii) from 0.8 to 1.5 mole part(s) of aliphatic polyamine having one and only one primary or secondary amino group in the molecule capable of participating in the Mannich condensation reaction; and (iii) from 0.8 to 1.3 mole part(s) of aldehyde, provided that the mole ratio of aldehyde to amine is 1.2:1 or less. Carrier fluids such as poly(oxyalkylene) compounds further enhance the effectiveness of these Mannich condensation products in minimizing or reducing intake valve deposits and/or intake valve sticking.

EP 0 870 819 A2

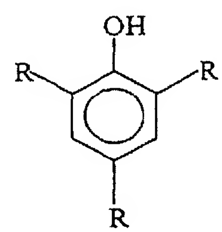
dispersity in the range of about 1 to about 4, from 0.8 to 1.2 mole part(s) of one or more N,N-dialkyl-α,ω-alkylene-diamines in which the alkylene group has at least 3 carbon atoms, and from 0.8 to 1.2 mole parts of formaldehyde, provided the mole ratio of formaldehyde to the diamine(s) is 1.2:1 or less. Because of outstanding effectiveness in control (i.e., reduction or minimization) of the weight of deposits formed on intake valves during engine operation, an especially preferred embodiment involves use of N,N-dimethyl-1,3-propanediamine as the polyamine, formaldehyde as the aldehyde, and a molar ratio of the above substituted phenol to N,N-dimethyl-1,3-propanediamine to formaldehyde of 1:1-1.15:0.90-1.20, respectively, with the proviso that if the molar quantity of formaldehyde is larger than the molar quantity of the amine, the excess molar amount of the formaldehyde does not exceed about 0.1. The most preferred molar ratio for these last-named reactants is about 1 mole of the N,N-dimethyl-1,3-propanediamine and about 1.05 mole of formaldehyde per mole of the above substituted phenol. Such Mannich base reaction products have given superlative results in an extensive number of tests.

Other embodiments and features of this invention will become still further apparent from the ensuing description and appended claims.

FURTHER DETAILED DESCRIPTION

Mannich Base Reaction Product

Representative high molecular weight substituted hydroxyaromatic compounds used in forming the present Mannich base products are represented by the following formula:



in which R is H, C_{1-4} alkyl, or a hydrocarbyl substituent having a number average molecular weight in the range of about 500 to about 3000, with the proviso that one R is H, one R is a C_{1-4} alkyl and one R is a hydrocarbyl substituent. It has been discovered that by using a substituted phenol which has only one site for the Mannich reaction to occur, i. e., only one ortho- or para-position being unsubstituted, products are obtained which are more effective at reducing intake valve deposits on an active/active basis compared to Mannich base products derived from a hydroxyaromatic compound having two or three reactive sites. Further, the Mannich base products of the present invention can be made in higher yields compared to products made from a hydroxyaromatic compound substituted in only one position.

Representative hydrocarbyl substituents include polypropylene, polybutene, polyisobutylene, and copolymers of butylene and propylene). Other similar long-chain hydrocarbyl substituents may be used, but are less preferred. Examples include copolymers of butylene and/or isobutylene and/or propylene, and one or more mono-olefinic comonomers copolymerizable therewith (e.g., ethylene, 1-pentene, 1-hexene, 1-octene, 1-decene, etc.) where the copolymer molecule contains at least 50 % by weight, of butylene and/or isobutylene and/or propylene units. The comonomers polymerized with propylene or such butenes may be aliphatic and can also contain non-aliphatic groups, e.g., styrene, o-methylstyrene, p-methylstyrene, divinyl benzene and the like. Thus in any case the resulting polymers and copolymers used in forming the substituted phenolic reactant are substantially aliphatic hydrocarbon polymers. Polybutylene is preferred. Unless otherwise specified herein, the term "polybutylene" is used in a generic sense to include polymers made from "pure" or "substantially pure" 1-butene or isobutene, and polymers made from mixtures of two or all three of 1-butene, 2-butene and isobutene. Commercial grades of such polymers may also contain insignificant amounts of other olefins. So-called high reactivity polybutylenes having relatively high proportions of polymer molecules having a terminal vinylidene group, i.e. at least 20% of the total olefin comprises an alkylvinylidene isomer, preferably at least 50% and more preferably at least 70%, formed by methods such as described, for example, in U.S. Pat. No. 4,152,499 and W. German Offenlegungsschrift 29 04 314, are also suitable for use in forming the long chain substituted phenol reactant.

The alkylation of the substituted hydroxyaromatic compound is typically performed in the presence of an alkylating catalyst such as BF_3 at a temperature in the range of about 50 to about 200°C.- The long chain alkyl substituents on the benzene ring of the phenolic compound are derived from polyolefin having a number average molecular weight

ducting the reaction on a large scale care should be exercised to compensate for any such losses so that the liquid reaction mixture actually contains the reactants in the proportions utilized pursuant to this invention.

Liquid Carriers

The Mannich base products of this invention are preferably used in combination with a liquid carrier or induction aid. Such carriers can be of various types, such as for example liquid poly-α-olefin oligomers, liquid polyalkene hydrocarbons (e.g., polypropene, polybutene, polyisobutene, or the like), liquid hydrotreated polyalkene hydrocarbons (e.g., hydrotreated polypropene, hydrotreated polybutene, hydrotreated polyisobutene, or the like), mineral oils, liquid poly(oxyalkylene) compounds, liquid alcohols or polyols, liquid esters, and similar liquid carriers or solvents. Mixtures of two or more such carriers or solvents can be employed.

Preferred liquid carriers because of their performance capabilities are 1) a mineral oil or a blend of mineral oils that have a viscosity index of less than about 120 , 2) one or a blend of poly-α-olefin oligomers, 3) one or more poly (oxyalkylene) compounds having an average molecular weight in the range of about 500 to about 3000, or 4) a mixture of any two or all three of 1), 2) and 3). The mineral oil carriers that can be used include paraffinic, naphthenic and asphaltic oils, and can be derived from various petroleum crude oils and processed in any suitable manner. For example, the mineral oils may be solvent extracted or hydrotreated oils. Reclaimed mineral oils can also be used. Hydrotreated oils are the most preferred. Preferably the mineral oil used has a viscosity at 40°C of less than about 1600 SUS, and more preferably between about 300 and 1500 SUS at 40°C. Paraffinic mineral oils most preferably have viscosities at 40°C in the range of about 475 SUS to about 700 SUS. For best results it is highly desirable that the mineral oil have a viscosity index of less than about 100, more preferably, less than about 70 and most preferably in the range of from about 30 to about 60.

The poly-α-olefins (PAO) which are included among the preferred carrier fluids are the hydrotreated and unhydrotreated poly-α-olefin oligomers, i.e., hydrogenated or unhydrogenated products, primarily trimers, tetramers and pentamers of α-olefin monomers, which monomers contain from 6 to 12, generally 8 to 12 and most preferably about 10 carbon atoms. Their synthesis is outlined in Hydrocarbon Processing, Feb. 1982, page 75 et seq., and in U.S. Pat. Nos. 3,763,244; 3,780,128; 4,172,855; 4,218,330; and 4,950,822. The usual process essentially comprises catalytic oligomerization of short chain linear alpha olefins (suitably obtained by catalytic treatment of ethylene). The poly-α-olefins used as carriers will usually have a viscosity (measured at 100°C) in the range of 2 to 20 centistokes (cSt). Preferably, the poly-α-olefin has a viscosity of at least 8 cSt, and most preferably about 10 cSt at 100°C.

The poly(oxyalkylene) compounds which are among the preferred carrier fluids for use in this invention are fuel-soluble compounds which can be represented by the following formula

$$R_1\text{-}(R_2\text{-}0)_n\text{-}R_3$$

wherein R_1 is typically a hydrogen, alkoxy, cycloalkoxy, hydroxy, amino, hydrocarbyl (e.g., alkyl, cycloalkyl, aryl, alkylaryl, aralkyl, etc.), amino-substituted hydrocarbyl, or hydroxy-substituted hydrocarbyl group, R_2 is an alkylene group having 2-10 carbon atoms (preferably 2-4 carbon atoms), R_3 is typically a hydrogen, alkoxy, cycloalkoxy, hydroxy, amino, hydrocarbyl (e.g., alkyl, cycloalkyl, aryl, alkylaryl, aralkyl, etc.), amino-substituted hydrocarbyl, or hydroxy-substituted hydrocarbyl group, and n is an integer from 1 to 500 and preferably in the range of from 3 to 120 representing the number (usually an average number) of repeating alkyleneoxy groups. In compounds having multiple $-R_2-O-$ groups, R_2 can be the same or different alkylene group and where different, can be arranged randomly or in blocks. Preferred poly(oxyalkylene) compounds are monools comprised of repeating units formed by reacting an alcohol with one or more alkylene oxides, preferably one alkylene oxide.

The average molecular weight of the poly(oxyalkylene) compounds used as carrier fluids is preferably in the range of from about 500 to about 3000, more preferably from about 750 to about 2500, and most preferably from above about 1000 to about 2000.

One useful sub-group of poly(oxyalkylene) compounds is comprised of the hydrocarbyl-terminated poly(oxyalkylene) monools such as are referred to in the passage at column 6, line 20 to column 7 line 14 of U.S. Pat. No. 4,877,416 and references cited in that passage, said passage and said references being incorporated herein by reference as if fully set forth.

A preferred sub-group of poly(oxyalkylene) compounds is comprised of one or a mixture of alkylpoly(oxyalkylene) monools which in its undiluted state is a gasoline-soluble liquid having a viscosity of at least about 70 centistokes (cSt) at 40°C and at least about 13 cSt at 100°C. Of these compounds, monools formed by propoxylation of one or a mixture of alkanols having at least about 8 carbon atoms, and more preferably in the range of about 10 to about 18 carbon atoms, are particularly preferred.

The poly(oxyalkylene) carriers used in the practice of this invention preferably have viscosities in their undiluted

engine. Thus the fuels will contain minor amounts of the Mannich base detergent/dispersant and of the liquid carrier fluid proportioned as above that control or reduce formation of engine deposits, especially intake system deposits, and most especially intake valve deposits in spark-ignition internal combustion engines. Generally speaking the fuels of this invention will contain on an active ingredient basis as defined above, an amount of the Mannich base detergent/ dispersant in the range of about 5 to about 150 ptb (pounds by weight of additive per thousand barrels by volume of fuel), and preferably in the range of about 10 to about 100 ptb. In the preferred fuel compositions wherein a liquid carrier fluid is used, the amount of the liquid carrier fluid will usually fall in the range of about 5 ptb to about 225 ptb, and preferably will be in the range of about 10 ptb to about 150 ptb. Other additives, such as one or more fuel-soluble antioxidants, demulsifying agents, rust or corrosion inhibitors, metal deactivators, combustion modifiers, alcohol co-solvents, octane improvers, emission reducers, friction modifiers, lubricity additives, ancillary detergent/dispersant additives, marker dyes, and multifunctional additives (e.g., methylcyclopentadienyl manganese tricarbonyl and/or other cyclopentadienyl manganese tricarbonyl compounds) can also be included in the fuels of this invention. These manganese compounds are among particularly preferred additional additives in the compositions of this invention because of their outstanding ability to reduce tailpipe emissions such as NOx and smog forming precursors, and to significantly improve the octane quality of fuel compositions, such as gasolines of the traditional types and of the newer "reformulated" types. Whatever components are selected for use in the compositions of this invention, each component should be present in an amount at least sufficient for it to exert its intended function or functions in the finished fuel composition.

The base fuels used in formulating the fuels of this invention are any and all base fuels suitable for use in the operation of spark ignition internal combustion engines such as unleaded motor and aviation gasolines, and so-called reformulated gasolines which typically contain both hydrocarbons of the gasoline boiling range and fuel-soluble oxygenated blending components such as alcohols, ethers, and other suitable oxygen-containing organic compounds. Preferred blending agents include fuel-soluble alkanols such as methanol, ethanol, and their higher homologs, and fuel-soluble ethers such as methyl tertiary butyl ether, ethyl tertiary butyl ether, methyl tertiary amyl ether, and analogous compounds, and mixtures of such materials. Oxygenates, when used, will normally be present in the base fuel in an amount below about 25 % by volume, and preferably in an amount that provides an oxygen content in the overall fuel in the range of about 0.5 to about 5 percent by volume. However in the practice of this invention departures from these ranges of proportions are permissible whenever deemed necessary, appropriate or desirable.

The additives used in formulating the preferred fuels of this invention can be blended into the base fuel individually or in various subcombinations. However, it is definitely preferable to blend all of the components concurrently using an additive concentrate of this invention as this takes advantage of the mutual compatibility afforded by the combination of ingredients when in the form of an additive concentrate. Also use of a concentrate reduces blending time and lessens the possibility of blending errors.

EXAMPLES

The practice and advantages of this invention are demonstrated by the following examples which are presented for purposes of illustration and not limitation. In each Mannich condensation reaction the following general procedure was used. The Mannich reaction products of the present invention were derived by reaction among long chain alkylated ortho-cresol ("PBP"), N,N-dimethyl-1,3-propanediamine ("DMPD"), and formaldehyde ("FA"). The PBP was formed by reacting ortho-cresol with a polyolefin indicated in Table 2. The Mannich reaction products outside of the scope of the present invention were derived by reaction among long chain alkylated phenol ("PBP"), DMPD or diethylene triamine ("DETA"), and FA. The PBP and DMPD/DETA were added to a resin kettle equipped with mechanized stirring, nitrogen feed, a Dean-Stark trap, and a heating mantle. Solvent, Aromatic 100 at 25 % by weight of product, was introduced and the mixture was heated to 50°C along with a slight exotherm. Next, 37 % formaldehyde solution was added gradually, while vigorous stirring was maintained. A second, mild exotherm was noted. The reaction mixture was heated to reflux; about 102°C. The azeotropic blend of water and solvent was removed continuously over a period lasting one hour. The temperature was increased as required to sustain removal of water, then the reaction mixture was heated gradually to 150°C, while sparging with nitrogen. After reaction the viscous product mixture was weighed and diluted with Aromatic 100 solvent as desired.

The activity of the product mixtures was determined by chromatographic separation. A 2-gram sample is separated on a silica gel column (40g of 60-200 mesh). The inactive components and alkylphenols are eluted from the column with n-hexane (400mL) and methylene chloride (400mL) respectively. The active Mannich components adhere to the gel, and can only be quantified by difference after all of the eluants are evaporated to dryness. The percentage of converted polyalkylphenol is calculated directly from the activity of the starting material and the weight fraction of polyalkylphenol in the product. Conversions for each example are given in Table 2. "PBP Activity" indicates how much of the polyolefin was reacted onto the hydroxyaromatic compound to form a substituted hydroxyaromatic compound. "% PBP Conversion" indicates how much of the substituted hydroxyaromatic compound reacted with the amine to form the Mannich product.

TABLE 2

Ex. No.	Polyolefin	Head Group	Amine	PBP Activity	% PBP Conversion	Carrier	Mannich, ptb	Carrier, ptb	IVD, mg	Fuel
1*	PIB	phenol	DMPD	76.16	87.85	D-21	40	32	108.10	A
2	HR-PIB	cresol	DMPD	88.39	94.34	D-21	32.1	32	33.30	A
3*	PIB	phenol	DMPD	76.16	85.93	D-21	39.6	32	41.90	B
4*	HR-PIB	phenol	DMPD	88.39	91.80	D-21	35.3	32	42.00	B
5	HR-PIB	cresol	DMPD	88.39	94.34	D-21	32.1	32	17.20	B
6	PIB	cresol	DMPD	74.5	91.77	AF-22	32.39	35	44.50	C
7*	PP	phenol	DETA	76.3	N/A	AF-22	35	35	75.40	C
8*	none	none	none	N/A	N/A	none	none	none	271	C

* Comparative Examples

Upon examination of Table 2, it is clear that the PBPs prepared from HR-PIB (Examples 2, 4*, and 5) exhibit significantly higher values for PBP activity than PBPs prepared from either PIB or PP (Examples 1*, 3*, 6, and 7), regardless of the head group, i.e., cresol or phenol. This indicates that more of the polyolefin is reacted onto the head group when HR-PIB is used compared to PBPs where PIB or PP are used. Further, upon reaction of the PBP with

4. A composition in accordance with Claim 1 or Claim 2 wherein the hydroxyaromatic compound is a substituted phenol in which the hydrocarbyl substituent is derived from polypropylene, polybutylene or a copolymer of propylene and butylene having a number average molecular weight in the range of about 500 to about 3000 and a polydispersity in the range of about 1 to about 4, wherein the polyamine is N,N-dimethyl-1,3-propanediamine, wherein the aldehyde is formaldehyde, and wherein the mole ratio of the substituted phenol to N,N-dimethyl-1,3-propanediamine to formaldehyde used in forming said product composition is 1:1-1.15:0.90-1.20, respectively, with the proviso that if the molar quantity of formaldehyde used is larger than the molar quantity of the amine used, the excess molar amount of the formaldehyde does not exceed about 0.1.

5. A composition in accordance with Claim 4 wherein said mole ratio is about 1 mole of the N,N-dimethyl-1,3-propanediamine and about 1.05 mole of formaldehyde per mole of the substituted phenol.

6. A composition in accordance with any one of Claims 1 to 5 wherein the hydrocarbyl substituent (a) of the substituted phenol is derived from polybutylene and the C_{1-4} alkyl (b) is methyl.

7. A composition in accordance with Claim 6 wherein at least about 20 percent of the total polybutylene comprises an alkylvinylidene isomer.

8. A fuel additive composition which comprises:

   a) a detergent/dispersant fuel-soluble Mannich product composition according to any one of Claims 1 to 7, and
   b) at least one liquid carrier for said detergent/dispersant in proportions such that for each part by weight of detergent/dispersant on an active ingredient basis there is in the range of about 0.3 to about 2.0 parts by weight of liquid carrier therefor.

9. A composition in accordance with Claim 8 wherein the liquid carrier is at least one fuel-soluble poly(oxyalkylene) compound.

10. A composition in accordance with Claim 9 wherein the weight ratio of said at least one poly(oxyalkylene) compound to the detergent/dispersant on an active ingredient basis is 2.0:1.0 or less.

11. A composition in accordance with Claim 9 or 10 wherein said poly(oxyalkylene) compound is at least one poly (oxypropylene) monool from 1,2-propylene oxide and one or more primary alcohols having at least 8 carbon atoms per molecule.

12. A composition in accordance with Claim 11 wherein said at least one monool has a kinematic viscosity in its undiluted state of at least 70 cSt at 40°C and at least about 13 cSt at 100°C.

13. A composition in accordance with any one of Claims 8 to 12 further comprising at least one inert hydrocarbon solvent that has a boiling point or boiling range below about 200°C.

14. A fuel composition for use in spark ignition internal combustion engines into which has been blended from about 5 to about 200 ptb of a composition of any one of Claims 1 to 7.

15. A fuel composition for use in spark ignition internal combustion engines into which has been blended a detergent/dispersant composition in accordance with any one of Claims 8 to 13 in an amount at least sufficient to reduce or minimize the weight of intake valve deposits in a spark ignition internal combustion engine operated on said fuel composition.

16. A method of minimizing or reducing intake valve deposits in a spark ignition internal combustion engine which comprises providing as fuel for the operation of the engine, a fuel composition in accordance with Claim 15.

17. A method of minimizing or reducing intake valve sticking in a spark ignition internal combustion engine which comprises providing as fuel for the operation of the engine, a fuel composition in accordance with Claim 15.

18. A Mannich product composition formed (A) one mole part of at least one substituted hydroxyaromatic compound having on the ring both (a) an aliphatic hydrocarbyl substituent derived from a polyolefin having a number average molecular weight in the range of about 500 to about 3000, and (b) a C_{1-4} alkyl; (B) from 0.8 to 1.3 mole part(s) of

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 870 819 A3

(12) EUROPEAN PATENT APPLICATION

(88) Date of publication A3:
16.06.1999 Bulletin 1999/24

(51) Int Cl.[6]: C10L 1/22, C10L 1/14, C10L 10/00

(43) Date of publication A2:
14.10.1998 Bulletin 1998/42

(21) Application number: 98302812.7

(22) Date of filing: 09.04.1998

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 10.04.1997 US 837246

(71) Applicant: ETHYL CORPORATION
Richmond, Virginia 23219-4304 (US)

(72) Inventors:
- Malfer, Dennis J.
  Glen Allen, Virginia 23060 (US)
- Franklin, Randall M.
  Mechanicsville, Virginia 23116 (US)
- Colucci, William L.
  Glen Allen, Virginia 23060 (US)

(74) Representative: Smaggasgale, Gillian Helen et al
Mathys & Squire,
100 Gray's Inn Road
London WC1X 8AL (GB)

(54) Additives for minimizing intake valve deposits, and their use

(57) New, highly effective detergent/dispersants for use in spark ignition fuels are described. They are Mannich condensation products formed from (i) one mole part of at least one substituted hydroxyaromatic compound having on the ring both (a) an aliphatic hydrocarbyl substituent derived from a polyolefin having a number average molecular weight in the range of about 500 to about 3000, and (b) a C_{1-4} alkyl; (ii) from 0.8 to 1.5 mole part(s) of aliphatic polyamine having one and only one primary or secondary amino group in the molecule capable of participating in the Mannich condensation reaction; and (iii) from 0.8 to 1.3 mole part(s) of aldehyde, provided that the mole ratio of aldehyde to amine is 1.2:1 or less. Carrier fluids such as poly(oxyalkylene) compounds further enhance the effectiveness of these Mannich condensation products in minimizing or reducing intake valve deposits and/or intake valve sticking.

Printed by Jouve, 75001 PARIS (FR)

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 30 2812

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	US 4 116 644 A (JACKISCH ET AL.) 26 September 1978 * column 4, line 38 - column 5, line 39; claim 1 *	1-22	
A	CA 2 089 833 A (SHELL) 21 August 1993 * the whole document *	1-22	
A	GB 2 010 324 A (CHEVRON) 27 June 1979 * page 1, line 121 - line 122 * * page 3, line 1 - line 22 * * page 8, line 40 - line 41 *	1-22	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	27 April 1999	De La Morinerie, B

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03 82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 98 30 2812

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

27-04-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 440507 A	07-08-1991	US 5200103 A	06-04-1993
		CA 2034760 A	02-08-1991
		DE 69101564 D	11-05-1994
		DE 69101564 T	21-07-1994
		JP 4339894 A	26-11-1992
		KR 151592 B	01-10-1998
		US 5382698 A	17-01-1995
		US 5433874 A	18-07-1995
		US 5345002 A	06-09-1994
US 5334775 A	02-08-1994	AU 6664394 A	20-12-1994
		CA 2161418 A	08-12-1994
		DE 69416122 D	04-03-1999
		EP 0701577 A	20-03-1996
		WO 9428035 A	08-12-1994
US 3994698 A	30-11-1976	US 3948619 A	06-04-1976
		CA 966309 A	22-04-1975
		DE 2209579 B	26-07-1976
US 4116644 A	26-09-1978	NONE	
CA 2089833 A	21-08-1993	NONE	
GB 2010324 A	27-06-1979	US 4166726 A	04-09-1979
		AU 521424 B	01-04-1982
		AU 4121578 A	08-05-1980
		BE 872543 A	30-03-1979
		BR 7808275 A	14-08-1979
		CA 1114609 A	22-12-1981
		DE 2853543 A	21-06-1979
		FR 2411882 A	13-07-1979
		JP 1403916 C	09-10-1987
		JP 54087706 A	12-07-1979
		JP 62010279 B	05-03-1987
		NL 7812133 A,B,	19-06-1979
		PH 13904 A	27-10-1980
		SE 438687 B	29-04-1985
		SE 7812741 A	17-06-1979
		ZA 7806072 A	31-10-1979

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82